

How large is the effect of 1s correlation on the D_e , ω_e , and r_e of N_2 ? 026702

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The effect of N 1s correlation on the spectroscopic constants of N_2 is studied using the coupled-cluster singles and doubles approach with a perturbational estimate of the connected triples [CCSD(T)] and internally contracted multireference configuration interaction (ICMRCI) techniques. At the ICMRCI level, we obtain a 1s effect of +1.35 kcal/mol on the dissociation energy. However, the effect is found to be smaller when size-extensive methods are used. The 1s effects computed at the CCSD(T) and internally contracted averaged coupled-pair-functional (ICACPF) levels are in excellent agreement. Our best estimate for the effect of 1s correlation is +0.8 kcal/mol on D_e , +9 cm^{-1} on ω_e , and -0.002 Å on the bond length. Including our estimate for the effect of 1s correlation, we obtain a D_e of 227.1 using a correlation-consistent polarized-valence sextuple zeta basis set at the ICMRCI+Q level (where the +Q indicates that the Davidson correction has been included). Basis set incompleteness, which is estimated to be 0.7 ± 0.2 kcal/mol, is still the major source of error. The CCSD(T) ten-electron results are found to be in excellent agreement with those obtained at the ICACPF or ICMRCI+Q levels of theory.

I. INTRODUCTION

There have been two relatively recent, rather extensive, theoretical studies^{1,2} of the N_2 dissociation energy; the first is by Almlöf *et al.*¹ (ADTBS) and the second is by Werner and Knowles² (WK). While the results of these studies agreed in many ways, they differed on the magnitude of the effect of the 1s correlation. The ADTBS study assumed that the core-core correlation was constant and computed only the core-valence correlation contribution at the multireference configuration interaction (MRCI) level of theory. This produced a 1s effect of 0.7 kcal/mol. This value was in agreement with that computed by Ahlrichs and co-workers,³ who included both core-core and core-valence correlation, but used the single-reference based coupled-pair-functional (CPF) approach.⁴ WK also included both core-core and core-valence correlation, but within the internally contracted (IC) MRCI framework;⁵ their value for the effect of 1s correlation was 1.3 kcal/mol. This result was rather surprising in light of the agreement of the two previous studies. In addition, neglect of the core-core correlation, as was done by ADTBS, tends to overestimate core effects. Thus the results of WK were expected to be smaller, not larger than those of ADTBS.

While in this work we focus on the effect of N 1s correlation on the N_2 D_e , we also consider its effect on ω_e and r_e . We perform MRCI and ICMRCI calculations and estimate the effect of higher excitations using the multireference analog of the Davidson correction (denoted +Q) or the IC averaged CPF (ICACPF) approach.^{5,6} We also perform coupled-cluster singles and doubles calculations,⁷ which include a perturbational estimate of the triples, denoted CCSD(T).⁸ This method has proven reliable for a number of "difficult" systems⁹ and calibration of its performance on triply bonded systems is of interest.

II. METHODS

We use the (augmented) correlation-consistent polarized-valence [(aug-)cc-pV] sets developed by Dunning and co-workers.¹⁰ The triple-zeta (TZ), quadruple-zeta (QZ), and quintuple-zeta (5Z) sets are used. The basis set that we denote as cc-pV5Z+(*spd*) has a diffuse *s* (0.05), *p* (0.038), and *d* (0.099) function added to the Dunning cc-pV5Z basis set. Following the scheme of Dunning, we develop a cc-pV6Z basis set, which is tabulated in Table I; the size of the contracted cc-pV6Z set is [7s6p5d4f3g2h1i]. The cc-pVQZ set is modified to study the effect of 1s correlation. The seven inner 1s functions are contracted to two functions using the coefficients given by Dunning. The outer five *s* functions are uncontracted as are the six *p* functions. Two tight *d* and *f* functions are added to the (3d2f1g) polarization set given by Dunning. The exponents of the added functions are 8.315 and 24.37 for the *d* functions and 5.998 and 17.75 for the *f* functions. The basis set developed to treat both core and valence correlation, which is denoted CV, is of the form (12s6p5d4f1g)/[7s6p5d4f1g]. The completeness of this basis set is tested by replacing the innermost two *p* functions by three with exponents of 53.6719, 21.469, and 8.588. Only the pure spherical harmonic components of the basis functions are used.

The CCSD(T) calculations are based on self-consistent-field (SCF) orbitals. For infinite separation, spin-restricted atomic calculations are performed for the 4S state of the N atom. For the MRCI, ICMRCI, and ICACPF calculations, the orbitals are optimized using a CASSCF approach that has the 2*p* orbitals as active; this has been previously denoted as CAS(6).² While only the 2*p* orbitals are active in the CASSCF, the 2*s* and 2*p* orbitals are active in the MRCI calculations; this is denoted ICMRCI(10) or MRCI(10) to indicate that all ten valence electrons are active in the (IC)MRCI treatment.

TABLE I. The nitrogen cc-pV6Z basis set. For the *s* and *p* spaces, the exponents and contraction coefficients for the 1*s*, 2*s*, and 2*p* orbitals are given. When no contraction coefficients are given, the functions are uncontracted.

<i>s</i> ^a			<i>p</i> ^a	
Exponent	Coefficient (1 <i>s</i>)	Coefficient (2 <i>s</i>)	Exponent	Coefficient (2 <i>p</i>)
432 381.1	0.000 006	0.000 001	673.555 6	0.000 064
64 743.42	0.000 043	0.000 010	159.584 5	0.000 562
14 733.70	0.000 229	0.000 050	51.801 70	0.003 085
4 173.254	0.000 965	0.000 213	19.673 43	0.012 298
1 361.477	0.003 500	0.000 775	8.175 345	0.038 625
491.504 9	0.011 284	0.002 504	3.616 131	0.099 815
191.685 7	0.032 599	0.007 362	1.673 414	
79.454 99	0.083 230	0.019 286	0.789 246	
34.549 68	0.179 930	0.044 699	0.372 339	
15.586 73	0.304 955	0.086 048	0.174 038	
7.235 444	0.341 159	0.133 249	0.078 681	
1.369 728				
0.625 089				
0.274 819				
0.119 209				
The exponents for the polarization functions ^b				
<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>
7.678 080	4.008 073	4.063 200	2.779 253	2.222
1.333 000	1.670 030	1.693 000	1.158 022	
3.199 200	0.695 846	0.705 417		
0.555 417	0.289 936			
0.231 424				

^aThe (16*s* 11*p*) primitive set [H. Partridge, J. Chem. Phys. **90**, 1043 (1989)] is used with the contraction coefficients taken from the N ⁴*S* SCF orbitals.

^bOptimized even-tempered polarization sets with β fixed at 2.4.

When 1*s* correlation is included in the ICMRCI(10) calculations, the same reference list is used as in the ten-electron calculations. That is, the 1*s* orbitals are treated as inactive in the 14-electron ICMRCI calculations. Internal contraction is used in most calculations to keep the size of the MRCI calculations tractable. The effect of internal contraction is tested for the cc-pVQZ basis set by performing MRCI calculations. Note that our CASSCF/ICMRCI(10) treatment is the same as the CAS(6)/CMRCI(10) calculations of WK. In some calculations, only the 2*p* functions are in the active space at the MRCI level, but ten electrons are still correlated (i.e., the 2*σ_g* and 2*σ_u* orbitals are doubly occupied in all reference configurations); these calculations are denoted as MRCI(6) or ICMRCI(6). Infinite separation is treated using a supermolecule approach for the MRCI, ICMRCI, and ICACPF treatments.

The full ghost basis set is used when the basis set superposition error (BSSE) is computed.¹¹ The ICMRCI calculations are performed using the MOLPRO codes^{5,12} while the CCSD(T) calculations were performed using ACES II.¹³ The MRCI calculations are performed using the SEWARD¹⁴/SWEDEN¹⁵ program system.

III. RESULTS AND DISCUSSION

On the basis of atomic splittings, ADTBS argued that the MRCI(10) *D_e* results were superior to those obtained at the MRCI(10)+*Q* level, but that the MRCI(6)+*Q* was superior to the MRCI(6) level. The MRCI(10) and

MRCI(6)+*Q* *D_e* values were in good agreement, with the MRCI(10) value being slightly larger. WK used the ICMRCI(10) treatment, but noted that in a small basis set, the full CI(FCI) result was between the ICMRCI(6) and ICMRCI(10) results. That is, the ICMRCI(10) result probably overshoots the true answer.

In Table II we give the ²*D* – ⁴*S* and ²*P* – ⁴*S* atomic separations from calculations analogous to those used for N₂. The ICMRCI(10), ICMRCI(10)+*Q*, and ICMRCI(6)+*Q* results are in good agreement with experiment, but the best agreement is obtained at the ICMRCI(10)+*Q* level. In Tables III and IV, the two active spaces are compared using the cc-pVQZ and cc-pV5Z (+*spd*) basis sets. We find that the ICMRCI(10)+*Q* and ICMRCI(6)+*Q* *D_e* values are in excellent agreement; the ICMRCI(10) results are larger and the ICMRCI(6) re-

TABLE II. Summary of the N atomic splittings, in eV, computed using the cc-pV5Z+ (*spd*) basis set.

Method ^a	² <i>D</i> – ⁴ <i>S</i>	² <i>P</i> – ⁴ <i>S</i>
ICMRCI(6)	2.42	3.69
ICMRCI(6)+ <i>Q</i>	2.39	3.53
ICMRCI(10)	2.42	3.60
ICMRCI(10)+ <i>Q</i>	2.39	3.59
Expt. ^b	2.38	3.58

^aThe atomic calculations are labeled by the N₂ calculation to which they correspond.

^bC. E. Moore, *Atomic Energy Levels*, U.S. Natl. Bur. Stand. Circ. No. 467 (National Bureau of Standards, Washington, D.C., 1949).

TABLE III. Summary of the D_e values^a (in kcal/mol) with ten electrons correlated. The results in parentheses are for the MRCI approach, without internal contraction.

Basis	CCSD	CCSD(T)	ICMRCI(10)	ICMRCI(10)+Q	ICACPF(10)
cc-pVTZ	207.6	216.3	217.8	216.6	
aug-cc-pVTZ	209.1	218.0	219.5	218.2	
cc-pVQZ	213.7	222.8	224.1(223.3)	223.1(223.0 ^b)	
CV	214.2	223.3	224.5	223.6	223.6
aug-cc-pVQZ	214.6	223.7	225.0	224.0	
cc-pV5Z	215.8	225.0	226.2	225.3	
cc-pV5Z+(<i>spd</i>)			226.4	225.5	
cc-pV5Z+(<i>spd</i>)+BF(<i>spd</i>)			226.7	225.8	
cc-pV5Z+(<i>spd</i>)+ <i>i</i>			226.7	225.9	
aug-cc-pV5Z			226.7	225.8	
cc-pV6Z minus <i>i</i>			226.8	226.0	
cc-pV6Z			227.1	226.3	
			ICMRCI(6)	ICMRCI(6)+Q	
cc-pVQZ			222.7(222.7)	223.1(223.1)	
cc-pV5Z+(<i>spd</i>)			224.9	225.4	

^aFor comparison, the experimental D_e value (Ref. 18) is 228.4 kcal/mol.^bIf $E_{\text{corr}} \times (1 - C_0^2)$ is used for the Davidson correction, instead of $E_{\text{corr}} \times (1 - C_0^2)/C_0^2$, the D_e is 222.2 kcal/mol, where E_{corr} is the correlation energy and C_0^2 is the weight of the reference configurations in the final wave function.

sults are smaller. The ICMRCI(10)+Q dissociation energy is 0.9 kcal/mol smaller than the ICMRCI(10) result. This is only about twice the difference between the FCI and ICMRCI(10) found by WK in a very small basis set. If the overshoot computed in the small basis set carries over to the big basis set, the true result is between the ICMRCI(10) and ICMRCI(10)+Q results. However, it seems likely that the overshoot will grow with the total correlation energy and therefore the correct result is probably closer to the ICMRCI(10)+Q than the ICMRCI(10) result. We also use the ICACPF(10) level of theory and find the results to be very similar to those obtained with the ICMRCI(10)+Q approach. On the basis of the atomic separations, the FCI calculations of WK, and on the agreement between the ICMRCI(10)+Q and ICMRCI(6)+Q results, we believe that our best multiref-

erence results are those obtained at the ICMRCI(10)+Q level of theory.

A study of the convergence of D_e and r_e values as a function of basis set at the ten-electron level is also summarized in Tables III and IV. The MRCI(10) result for D_e is 0.8 kcal/mol smaller than the ICMRCI(10) result; this is similar to the difference found by WK (with a different basis set). However, the MRCI(6), MRCI(6)+Q, and MRCI(10)+Q results are in very good agreement with the corresponding internally contracted results. Note that the larger effect of the +Q correction in the MRCI(10) treatment reported by ADTBS is due to a different definition of the Davidson correction—see the footnote for Table III. Our ICMRCI(10) D_e value using the cc-pV5Z+(*spd*) basis set is the same as obtained by WK using the same polarization set, but a different *sp* set. Our

TABLE IV. Summary of the r_e values^a (in Å) with ten electrons correlated. The results in parentheses are for the MRCI approach, without internal contraction.

Basis	CCSD	CCSD(T)	ICMRCI(10)	ICMRCI(10)+Q	ICACPF(10)
cc-pVTZ	1.097	1.105	1.104	1.105	
aug-cc-pVTZ	1.097	1.105	1.104	1.105	
cc-pVQZ	1.094	1.101	1.101(1.101)	1.101(1.102)	
CV	1.093	1.100	1.100	1.101	1.101
aug-cc-pVQZ	1.094	1.101	1.101	1.102	
cc-pV5Z	1.093	1.100	1.100	1.101	
cc-pV5Z+(<i>spd</i>)			1.100	1.101	
cc-pV5Z+(<i>spd</i>)+BF(<i>spd</i>)			1.100	1.101	
cc-pV5Z+(<i>spd</i>)+ <i>i</i>			1.100	1.100	
aug-cc-pV5Z			1.100	1.100	
cc-pV6Z minus <i>i</i>			1.100	1.100	
cc-pV6Z			1.100	1.100	
			ICMRCI(6)	ICMRCI(6)+Q	
cc-pVQZ			1.100(1.101)	1.101(1.102)	
cc-pV5Z+(<i>spd</i>)			1.099	1.101	

^aFor comparison, the experimental r_e value (Ref. 18) is 1.0977 Å.

ICMRCI(10)+Q result in the cc-pV5Z+(*spd*) basis set is 1.0 kcal/mol larger than the value obtained by ADTBS in their [6s5p4d3f2g1h] atomic natural orbital¹⁶ (ANO) basis set. This difference is due to an overcontraction of the valence space in the ANO basis set (0.46 kcal/mol), the absence of diffuse functions in the ANO set (0.16 kcal/mol), and the MRCI(6)+Q vs the ICMRCI(10)+Q treatments (0.38 kcal/mol); the former two quantities are taken from the work of WK. Thus our ICMRCI results are consistent with those obtained previously^{1,2} using slightly different basis sets and/or correlation treatments.

Our ICMRCI(10) D_e value obtained at the cc-pV6Z level is larger than the best value reported by WK using a basis set similar to the cc-pV5Z+(*spd*) basis set with an *i* function added. We have therefore investigated the increase in the dissociation energy between the cc-pV5Z and cc-pV6Z basis set in some detail. First adding an *i* function to the cc-pV5Z+(*spd*) set increases the D_e by 0.3 and 0.4 kcal/mol for the ICMRCI(10) and ICMRCI(10)+Q levels of theory, respectively. The former value is the same as reported by WK and the latter value is similar to that reported by ADTBS. The importance of the *i* functions can also be computed by removing the *i* functions from the cc-pV6Z basis, this again yields a very similar result (0.3 kcal/mol). Adding a diffuse *f*, *g*, and *h* function to the cc-pV5Z+(*spd*) set, thus producing the aug-cc-pV5Z set (ignoring the small differences in the exponents of the diffuse *spd* functions), increases the D_e value by 0.5 kcal/mol, which is rather a sizable change.

In light of the magnitude of the changes between the cc-pV5Z and aug-cc-pV5Z and between the cc-pV5Z and cc-pV6Z basis sets, one would like to be able to consider basis sets larger than cc-pV6Z; unfortunately, this is not practical. Augmenting the cc-pV6Z basis set with a diffuse *s*, *p*, and *d* function leads to numerical problems, but based on the r values near r_e , the addition of these diffuse functions to the cc-pV6Z basis set increase the D_e by only about 0.03 kcal/mol. Thus, the cc-pV6Z basis set has become sufficiently diffuse that it is not necessary to add diffuse *spd* functions for the calculation of D_e . This is supported by the virtually identical binding energies obtained at the ICMRCI(10)+Q level by replacing the *spd* set from the cc-pV5Z+(*spd*) set with the *spd* functions from the cc-pV6Z set. However, as noted above, most of the basis set incompleteness is in the higher angular momentum spaces. Successively replacing the *f*, *g*, and *h* functions in the cc-pV5Z set by those in the cc-pV6Z set increases the D_e by 0.10, 0.15, and 0.24 kcal/mol, respectively. The magnitude of these *l*-value saturation effects is surprisingly large and when coupled with the size of the *i* effect indicates that much of the remaining error in the computed D_e is due to basis set incompleteness.

While plots of the D_e vs basis set size did not yield any insight into the magnitude of the remaining error, we have observed that plotting the increase in D_e with basis set improvement for the cc-pVnZ series (for $n=T, Q, 5$, and 6) has a nearly exponential falloff. This allows us to estimate the remaining basis set incompleteness in the cc-pV6Z set for a valence correlation treatment. This ap-

proach yields a basis set limit of 227.0 and 227.9 kcal/mol for the ICMRCI(10)+Q and ICMRCI(10) levels of theory, respectively. We estimate this extrapolation to be accurate to ± 0.2 kcal/mol. It is somewhat disappointing that basis set incompleteness in the cc-pV6Z basis set (0.7 ± 2 kcal/mol) is so much larger than the BSSE (0.2 kcal/mol).

We should also note that we tried to estimate the basis set incompleteness by adding a set of *spd* bond functions (BF) to the cc-pV5Z+(*spd*) set. The exponents of these BF were optimized for N₂ at r_e in conjunction with the cc-pVTZ basis set. The bond functions increase the D_e of the cc-pV5Z+(*spd*) basis set by only 0.3 kcal/mol (0.2 kcal/mol, accounting for the increase in the BSSE). This is compared with the 0.8 kcal/mol increase by going from the cc-pV5Z+(*spd*) to the cc-pV6Z basis set. We should further note that adding an *f* function to the BF set resulted in linear dependence problems. Thus bond functions appear to be a very inefficient method for improving the basis set once large atomic centered sets are used.

The CCSD results are not very good, with errors of 10 kcal/mol in the dissociation energy. However, once the triples correction is added, the results are only 0.2–0.3 kcal/mol smaller than the ICMRCI(10)+Q results. Thus the CCSD(T) is in excellent agreement with our best multireference treatment. As the +Q has only about a 1 kcal/mol effect, this conclusion is valid even if the true result falls between the ICMRCI(10) and ICMRCI(10)+Q values. A similar conclusion about the accuracy of the CCSD(T) approach was made by Scuseria,¹⁷ who compared his CCSD(T) results with the MRCI(6)+Q results of ADTBS.

On the basis of the results presented in Table III, the cc-pVQZ basis set was used as the starting point for the 1s correlation basis. As noted above, the *sp* space was recontracted and tight *d* and *f* functions were added. These changes slightly increase the dissociation energy at the ten-electron level. Using this CV basis set, both 10 and 14 electrons were correlated; the results of these calculations are summarized in Table V. The ICMRCI(10) calculations yield a 1s effect that is similar to, but slightly larger than, the effect found by WK. However, the effect of 1s correlation is much smaller using the size-extensive methods. While there might be some debate as to whether to use the ICMRCI(10) or the ICMRCI(10)+Q approach for the valence treatment, it seems highly desirable to have a size-extensive method when comparing calculations with different numbers of electrons correlated. Thus we conclude that the effect of 1s correlation is overestimated at the ICMRCI(10) level.

We have computed the BSSE for both five- and seven-electron correlation treatments. The inclusion of 1s correlation only slightly increases the BSSE. Thus, at all levels of theory, correcting the 1s effect on D_e for differential BSSE effects makes only a very small difference.

Possibly the largest limitation of the CV basis set is the inner *p* functions. This was tested using the basis set that replaces the inner two functions by three functions. Because of disk space requirements that arise during the cal-

TABLE V. Summary of the results using the CV basis set.

	CCSD	CCSD(T)	ICMRCI(10)	ICMRCI(10)+Q	ICACPF(10)
			$r_e(\text{\AA})$		
10- <i>e</i>	1.093	1.0999	1.1002	1.1009	1.1008 ^a
14- <i>e</i>	1.091	1.0978	1.0979	1.0988	1.0988 ^a
			BSSE(kcal/mol)		
10- <i>e</i>	0.52	0.58	0.54	0.58	0.56
14- <i>e</i>	0.58	0.64	0.56	0.60	0.60
			$D_e(\text{kcal/mol})$		
10- <i>e</i>	214.2	223.3	224.5	223.6	223.6
14- <i>e</i>	214.7	224.1	225.8	224.7	224.5
Δ	0.54	0.80	1.36	1.10	0.86
Δ -BSSE	0.48	0.74	1.34	1.08	0.82

^aThe ICACPF(10) bond lengths after correction for BSSE are 1.1010 and 1.0989 Å at the 10- and 14-electron levels, respectively.

culuation of the BSSE, this larger basis set could not be used in the CCSD(T) calculations, but was quite tractable in the ICMRCI(10) and ICACPF(10) calculations. This basis set improvement lowers the total energy of the 10- and 14-electron treatments by about 0.000 02 and 0.0008 E_h , respectively. It also reduces the differential BSSE effect with 1s correlation to less than 0.01 kcal/mol at the ICMRCI+Q and ICACPF levels. However, this hardly changes the effect of 1s correlation, which is 1.35, 1.03, and 0.85 kcal/mol at the ICMRCI(10), ICMRCI(10)+Q, and ICACPF(10) levels of theory, respectively.

On the basis of these calculations we believe that the effect of 1s correlation is less than 1.0 kcal/mol and probably about 0.8 kcal/mol. If we add this correction to our estimated basis set limit results for valence correlation we obtain 227.8 and 228.7 kcal/mol for the ICMRCI(10)+Q and ICMRCI(10) levels, respectively. The experimental result¹⁸ of 228.4 kcal/mol lies between these two values, which is consistent with the FCI result of WK. The difference between our computed values and experiment is of approximately the same size as the sum of our estimated uncertainty in the extrapolation to the basis set limit and in the size of the 1s effect, thus it is hard to assign the uncertainty due to the treatment of electron correlation. However, as noted below, the ICMRCI(10) results do not show a consistency in the sign of the errors of D_e , r_e , and ω_e , while the ICMRCI(10)+Q results do. This combined with the fact that our best ICMRCI(10)+Q value is smaller than experiment and our best ICMRCI(10) value is larger than experiment leads us to conclude that there is still a small error in our treatment of electron correlation. On the basis of our calculations, we think that WK achieved an error of only 0.5 kcal/mol in the N₂ D_e with the aid of some cancellation of errors; they overestimated the importance of 1s correlation, neglected BSSE, did not reach the one-particle basis set limit, and used the ICMRCI(10) approach, which probably overshoots the correct answer. However, our calculations show that it is very difficult to reach the one-particle limit without some extrapolation of the results.

The ICMRCI(10)+Q and ICMRCI(10) bond lengths determined using the CV basis set are only 0.0008 Å longer than those obtained using the cc-pV6Z basis set.

The effect of 1s correlation, while very small, slightly reduces the bond length. The 14-electron ICMRCI(10)+Q result of 1.0988 Å is in good agreement with the experimental value¹⁸ of 1.0977. Correcting this for basis set limitations in the ten-electron treatment leads to an error of only 0.0003 Å. Correcting the results for BSSE would only have a very small (+0.0001–0.0002 Å) effect. The CCSD(T) and ICMRCI(10) values obtained using the CV basis set of 1.0978 and 1.0979 Å, respectively, are in even better agreement with experiment. If the valence and BSSE corrections are applied, the CCSD(T) and ICMRCI(10) results would be shorter than experiment. We can conclude, however, that all three levels of correlation treatment are in good agreement with experiment once 1s correlation is added. Finally we note that the contraction in r_e due to 1s correlation, unlike the D_e , is similar at all levels of theory; we find contractions of 0.0021, 0.0023, 0.0021, and 0.0020 Å at the CCSD(T), ICMRCI(10), ICMRCI(10)+Q, and ICACPF(10) levels of theory, respectively. WK report essentially the same contraction (0.0022 Å) at the ICMRCI(10) level.

WK reported their best ω_e value as 2366.6 cm⁻¹, which is 8 cm⁻¹ larger than experiment; this result was obtained at the ICMRCI(10) level with 14 electrons correlated. With the addition of the +Q correction, their result (2358.0 cm⁻¹) was in excellent agreement with experiment¹⁸ (2358.6 cm⁻¹). They found the effect of 1s correlation on ω_e (computed using two slightly different basis sets for the 10- and 14-electron treatments) was about +11 cm⁻¹.

Lee and Rice¹⁹ computed an ω_e value of 2357 cm⁻¹ using a ten-electron CCSD(T) approach. Allen and Csaszar²⁰ computed that this would increase by about +26 cm⁻¹ if ω_e was evaluated at the experimental r_e value (see the discussion in Ref. 29 of the paper by Allen and Csaszar). This would appear to imply either that the effect of 1s correlation is to reduce ω_e by 24 cm⁻¹ or that a 14-electron CCSD(T) treatment in an infinite basis set will yield an ω_e value that is too large (i.e., the inner-shell effect works in the same direction as the valence level overshoot predicted by Allen and Csaszar). The former conclusion is in clear contrast to the results of WK, while the latter conclusion appears to be inconsistent with change in ω_e

TABLE VI. Summary of the results for ω_e , in cm⁻¹.

Method	Basis	10-electron	14-electron	Δ
ICMRCI(10)	cc-pV5Z+(<i>spd</i>)	2355.2		
ICMRCI(10)+Q	cc-pV5Z+(<i>spd</i>)	2348.1		
ICACPF(10)	CV	2346.1	2354.9	8.8
ICACPF(10)-BSSE	CV	2345.1	2353.8	8.7
CCSD(T)	CV	2357.2	2367.0	9.8
Expt. ^a			2358.6	

^aReference 18.

values with basis set improvement reported by Lee and Rice for a CCSD(T) treatment correlating ten electrons.

In light of the concern about using a size-extensive method to study the 1s effect and the result of Allen and Csaszar, we have also determined ω_e , which we compute by fitting an eighth-order polynomial to 13 or 14 points around r_e . While ω_e is the same to better than 0.1 cm⁻¹ if a sixth- or tenth-order polynomial is used, $\omega_e X_e$ shows small variations with the order of the polynomial used and is therefore not reported. Our results are summarized in Table VI.

Our ICMRCI(10) result in the cc-pV5Z+(*spd*) basis set is in very good agreement with experiment and with the ten-electron results of WK. The +Q correction reduces ω_e , also as found by WK. Using the CV basis set, we compute the effect of 1s correlation at the ICACPF(10) and CCSD(T) levels. We first note that the CCSD(T) ten-electron results are the same as those obtained by Lee and Rice using similar basis sets, and the ten-electron ICACPF(10) results are in good agreement with the ICMRCI(10)+Q results in the cc-pV5Z+(*spd*) basis set. The CCSD(T) and ICACPF(10) results for the effect of 1s correlation are in good agreement with each other and with the previous result of WK, leading to the conclusion that the effect of 1s correlation is to increase ω_e by about 9 cm⁻¹. Adding this correction to our ICMRCI(10)+Q result, obtained using the cc-pV5Z+(*spd*) basis set, leads to a value that is only 1.5 cm⁻¹ smaller than experiment. The error would be only 1 cm⁻¹ larger if the BSSE is also accounted for. If our 1s effect is added to the cc-pV5Z+(*spd*) ICMRCI(10) result, the value is larger than experiment. This is consistent with our view that the ICMRCI(10)+Q approach is a better approximation to the full CI than is the ICMRCI(10). We note that the 14-electron CCSD(T) result is also larger than experiment; it is possible that this is due to the fact that the SCF wave function, on which the CCSD(T) is based, does not correctly dissociate for N₂. The increase in ω_e between the 10- and 14-electron treatments is smaller than the shift in ω_e with r computed by Allen and Csaszar using only 10-electron results, even though the 14-electron CCSD(T) treatment result yields an r_e value that is in excellent agreement with experiment. The difference is probably due to the fact that 1s correlation results in a reasonably constant shift in r so that it changes the shape of the potential by far less than an analogous shift in r_e due to improvements in the valence treatment. As with the r_e , it is clear that all three correlation methods are very accurate.

Finally we note that for the ICMRCI(10)+Q and ICACPF(10) levels of theory the errors are in the expected order. Namely, the D_e and ω_e are too small and r_e is too large. For both the CCSD(T) and ICMRCI(10) levels of theory, D_e is too small, ω_e is too large, and r_e is too short. This consistency of the direction of the errors in D_e , r_e , and ω_e is further support for our preference for the ICMRCI(10)+Q results over those obtained at the ICMRCI(10) level.

IV. CONCLUSIONS

The CCSD(T) results for the N₂ dissociation energy are found to be in excellent agreement with those obtained at the ICMRCI+Q level; the difference is less than 0.5 kcal/mol for all basis sets considered. At the ICMRCI level, the effect of 1s correlation is computed to be 1.34 kcal/mol, which is similar to that reported by Werner and Knowles. However, when the size-extensive CCSD(T) or ICACPF methods are used, the effect of 1s correlation is smaller, 0.74 and 0.82 kcal/mol, respectively. These smaller values are a better estimate of the true 1s effect on the N₂ dissociation energy. While our best estimate for the 1s effect on D_e is smaller than that obtained previously, the 1s effect found in this work for r_e and ω_e are similar to those reported previously. The 1s correlation reduces the bond length by 0.002 Å and increases ω_e by 9 cm⁻¹, which brings the ICMRCI+Q values into better agreement with experiment. The 1s effect for ω_e does, however, lead to values for the CCSD(T) and ICMRCI approaches that are slightly larger than experiment. The basis set incompleteness is estimated to be 0.7±0.2 kcal/mol for the largest, [7s6p5d4f3g2h1i], basis set used. Thus the largest source of error in the calculation of the N₂ D_e appears to be due to limitations in the one-particle basis set.

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